U.S. DEPARTMENT OF ENERGY
OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

NUCLEAR WASTE TECHNICAL REVIEW BOARD
FULL BOARD MEETING

SUBJECT: DISSOLUTION TESTING OF SPENT FUEL

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OVERALL OBJECTIVE

Provide experimental source-term data and models that can be used to help predict the potential for release of radionuclides from a repository in the unlikely event that spent fuel is contacted by groundwater.

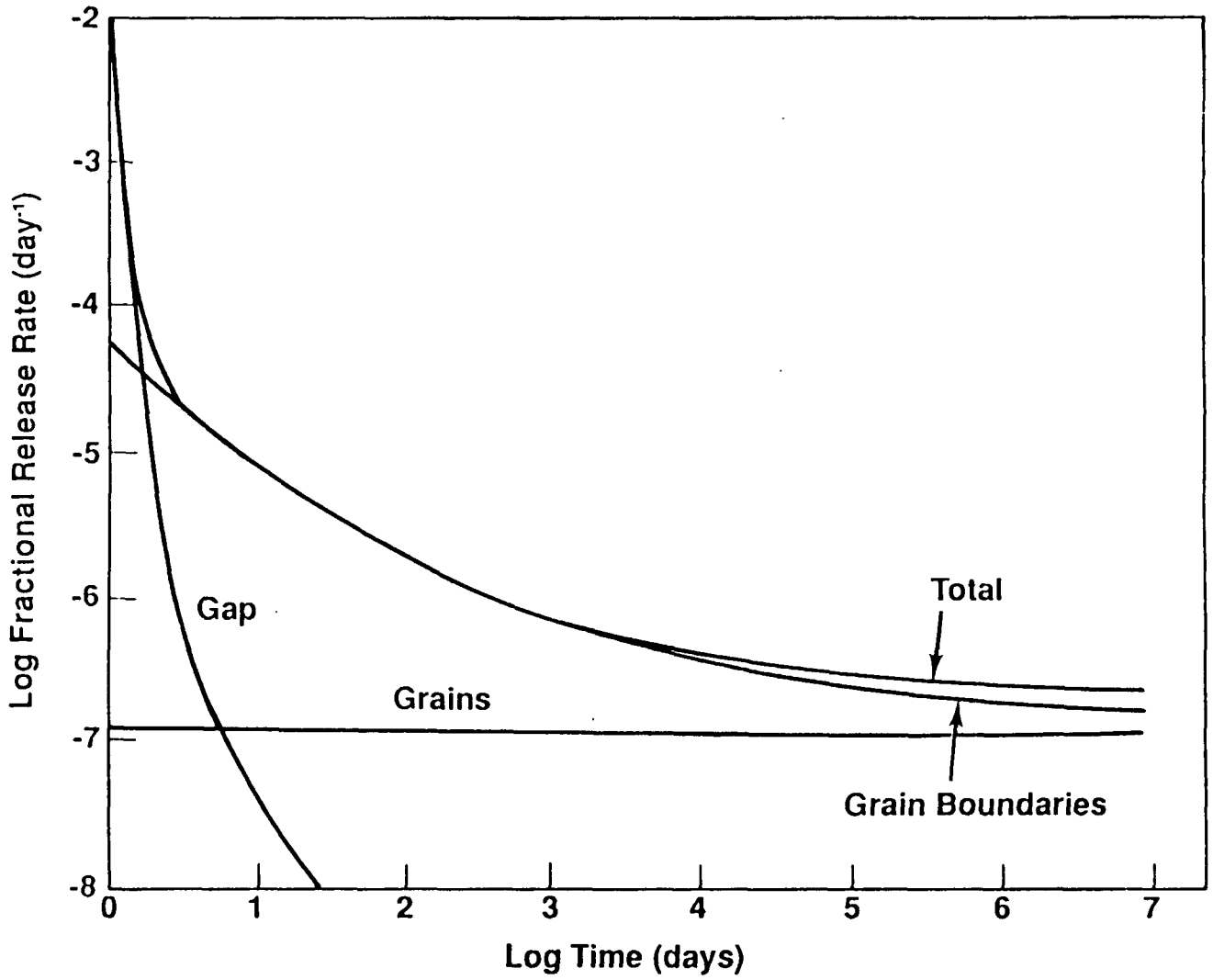
BACKGROUND

- Over 98% of the 1000-year radioactive inventory in spent fuel is Am and Pu.
  - * Release will be controlled by solubility (or possibly colloidal transport).
- Release of soluble radionuclides (^{99}Tc, ^{135}Cs, ^{129}I) will be controlled by two separate mechanisms because of the heterogeneous nature of spent fuel.
  - * Rapid release of Cs and I (0.1 to 20% of total inventories) from gap and grain boundaries.
  - * Long-term release of soluble radionuclides contained within the UO_2 matrix of spent fuel will be controlled by the dissolution rate of that matrix.

PWR Spent Fuel Radionuclide Inventories at 1,000 Years

Radionuclide	Half-Life (years)	1,000-Year Activity (% of Total)	Cumulative Activity (%)
^{241}Am	432	51.3	51.3
^{243}Am	7,380	1.8	53.1
^{240}Pu	6,570	27.4	80.5
^{239}Pu	24,100	17.5	98.0
^{242}Pu	375,800	0.10	98.1
^{238}Pu	88	0.06	98.1
^{99}Tc	213,000	0.75	98.9
^{135}Cs	2,300,000	0.020	
^{129}I	15,700,000	0.0018	

Soluble Fission-Product Release from UO_2 Fuel in Water Under Oxidizing Conditions



L. H. Johnson, N. C. Garisto, and S. Stroes-Gascoyne, in Waste Management '85, Vol. 1--High-Level Waste, pp. 479-482.

DATA NEEDS/MOTIVATION

- Thermodynamic data for key solid/solution reactions involving low-solubility radionuclides.

  * These radionuclides constitute most of the activity in spent fuel, and solubility will control their release unless colloids make an important contribution.

- Experiments to determine the nature and importance of actinide-bearing colloids.

- Gap inventories and grain-boundary inventories of soluble radionuclides.

  * YMP assumes immediate dissolution of gap and grain-boundary inventories upon contact by water--inventories must be measured.

DATA NEEDS/MOTIVATION (Continued)

- Demonstration that spent fuel matrix dissolves congruently.
  - * YMP assumes matrix dissolution controls dissolution of soluble radionuclides--this needs verification.
- Kinetics of spent fuel matrix dissolution as a function of water chemistry and fuel condition.
  - * Spent fuel dissolution mechanism is poorly understood.
  - * The effect of prior oxidation on dissolution is unknown.
  - * A better understanding of these factors is needed to predict the long-term release of soluble radionuclides.

ACCOMPLISHMENTS FY 1987 - 1992

- Completed three series of semi-static spent fuel dissolution tests; the first in deionized water; the second and third in J-13 water.
  - * Results are documented in HEDL-TME 84-30, PNL-7169 and PNL-7170
- Developed methods for:
  - * Preparing separated fuel-grain specimens, thus exposing grain boundaries and allowing inventories of radionuclides concentrated therein to be measured.
  - * Conducting flow-through dissolution-rate measurements.
- Measured gap and grain-boundary inventories of Cs, Tc, and Sr -- only two different fuels tested to date.
- Showed that spent fuel grains dissolve nearly congruently -- only three different fuels tested to date.
- Showed importance of Si and Ca in test solutions.

Summary of Results for Artificially Defected Cladding

- ^{137}Cs concentrations 2 to 4 times lower from defected rods compared to bare fuel tests.
- ^{99}Tc concentrations 20 to 40 times lower from defected rods compared to bare fuel tests.
- Actinide concentrations 100 to 1000 times lower from defected rods compared to bare fuel tests.

Annual Release Rates at 25°C in J-13 Water
as Fraction of 1,000-Year Inventories

Actinide	log(Release Rate)*
U	-8.6
Np	-8.8
Pu	-9.0
Am	-9.1

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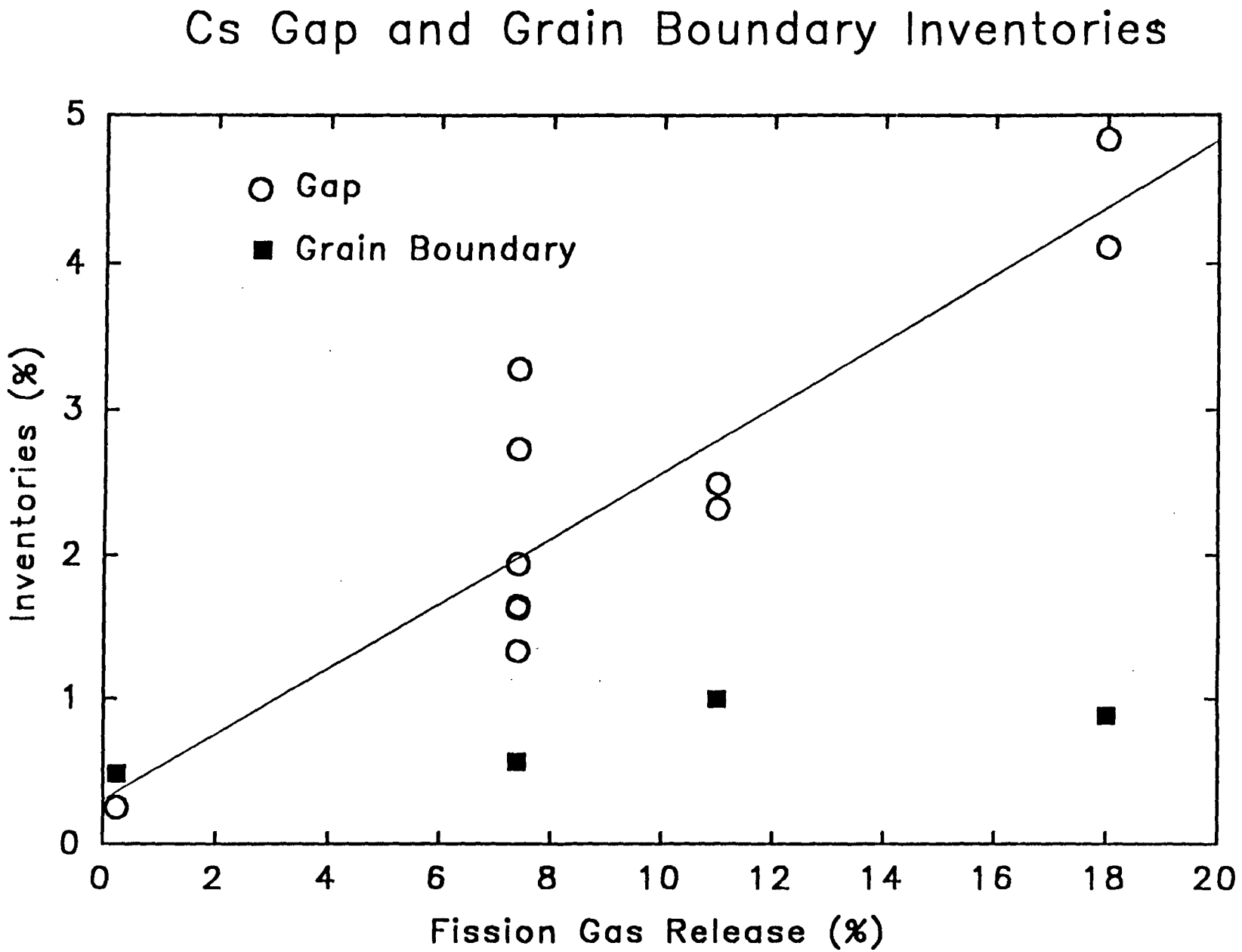
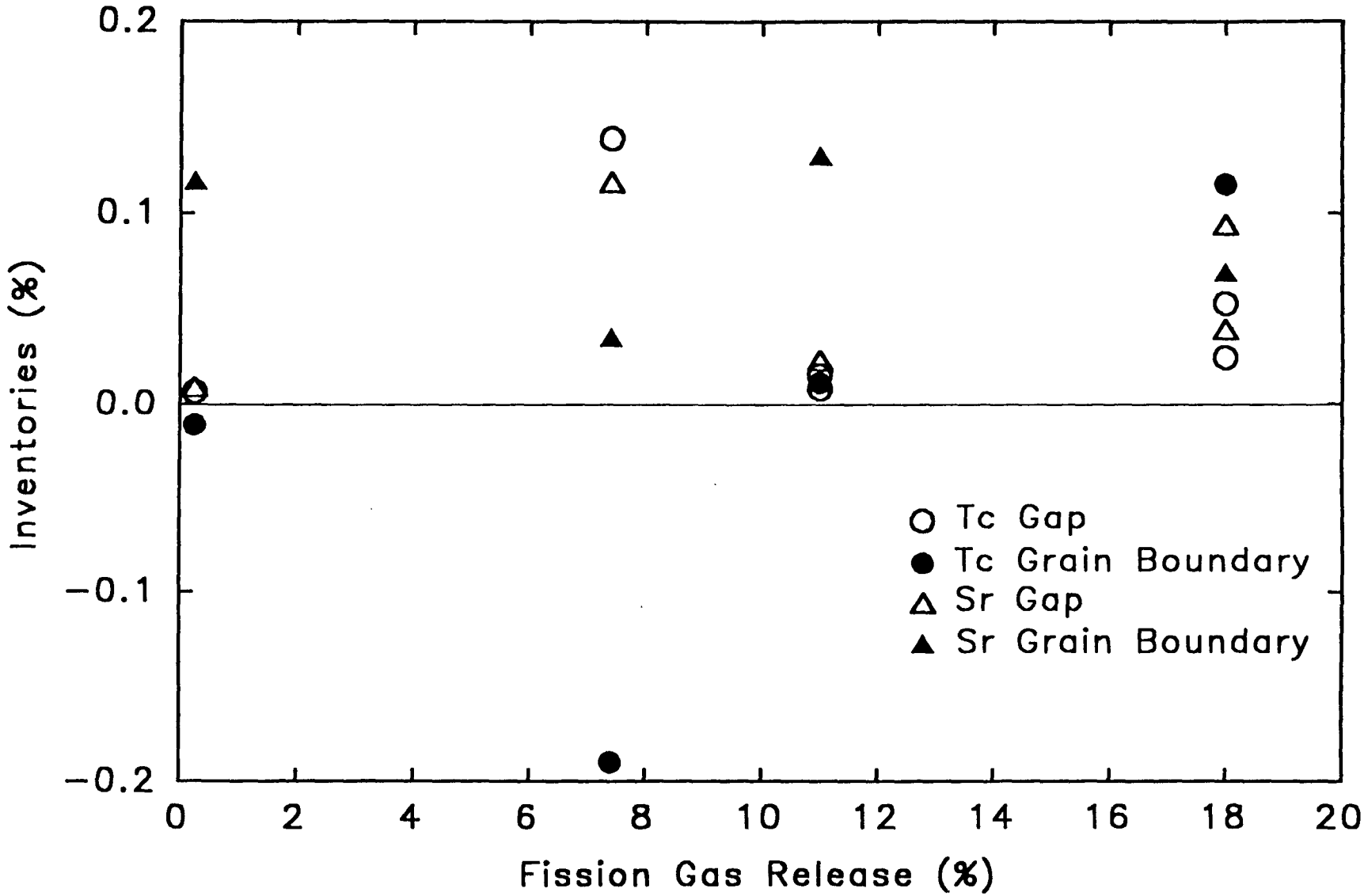
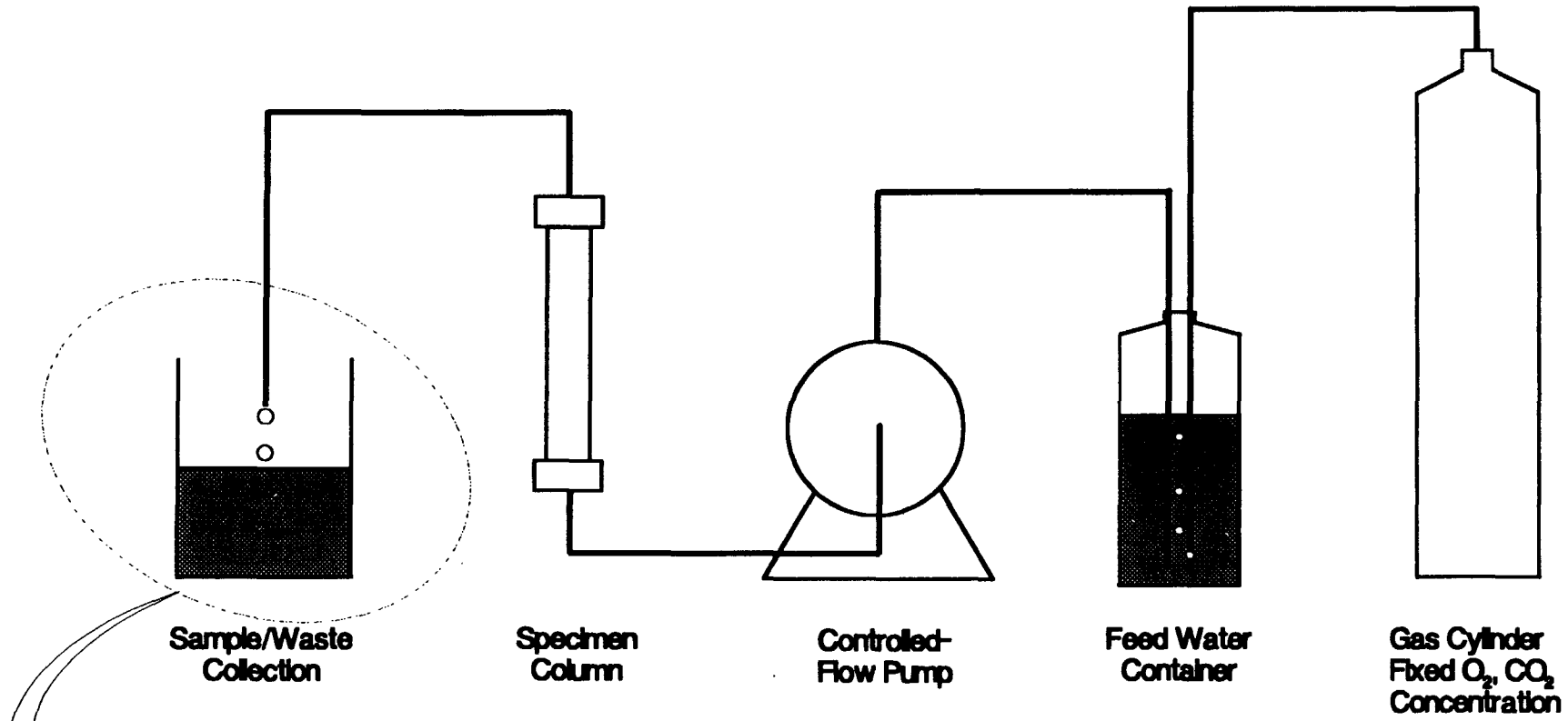
* Assumes water flow rate of 20 L/Yr per waste package containing 3140 kg of 33 MWd/kgM PWR fuel.


Cs Gap and Grain Boundary Inventories
Gap
Grain Boundary
Inventories (%)
Fission Gas Release (%)
0
1
2
3
4
5
0
2
4
6
8
10
12
14
16
18
20

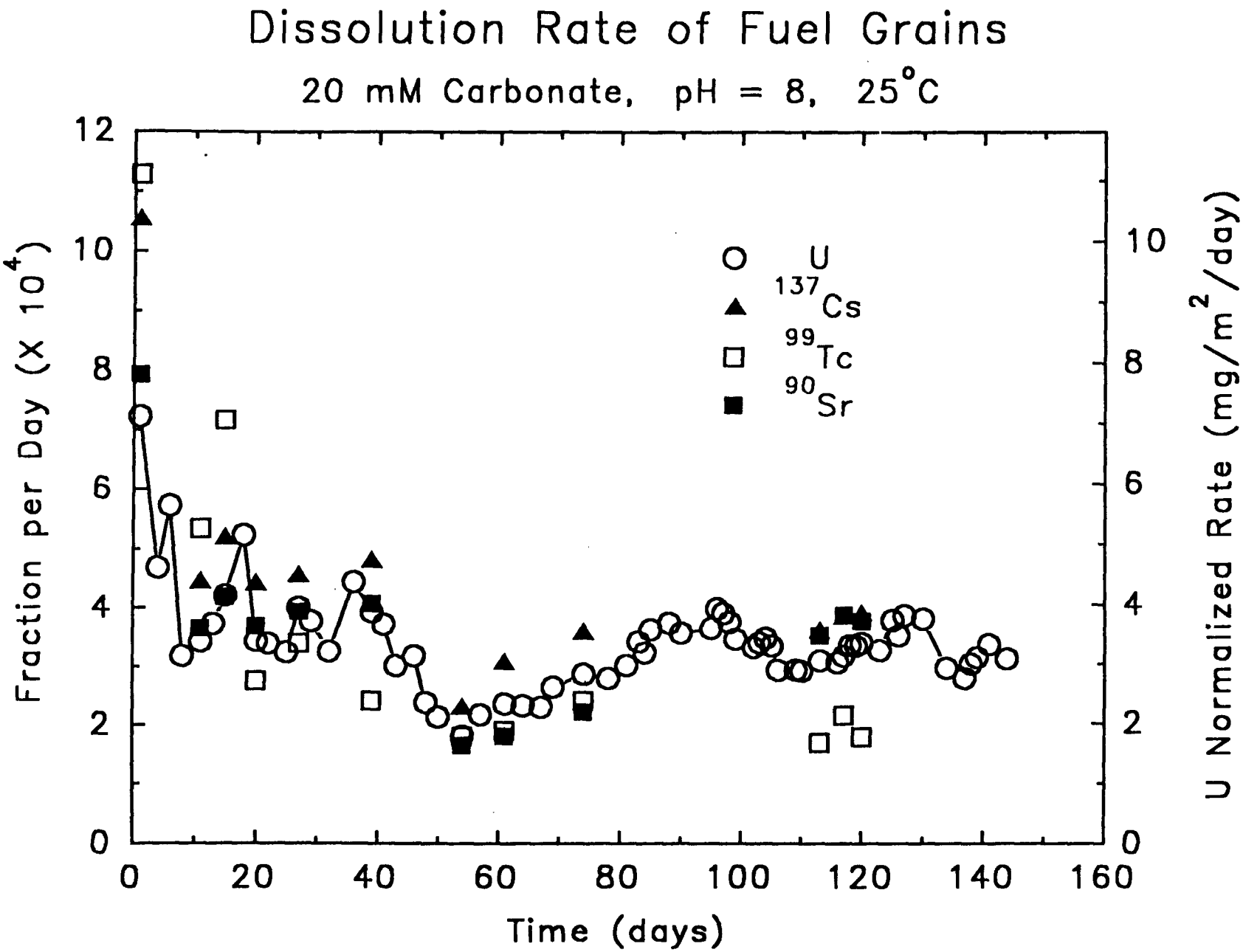

Tc & Sr Gap and Grain Boundary Inventories
0.2
0.1
0.0
−0.1
−0.2
Inventories (%)
0
2
4
6
8
10
12
14
16
18
20
Fission Gas Release (%)
Tc Gap
Tc Grain Boundary
Sr Gap
Sr Grain Boundary

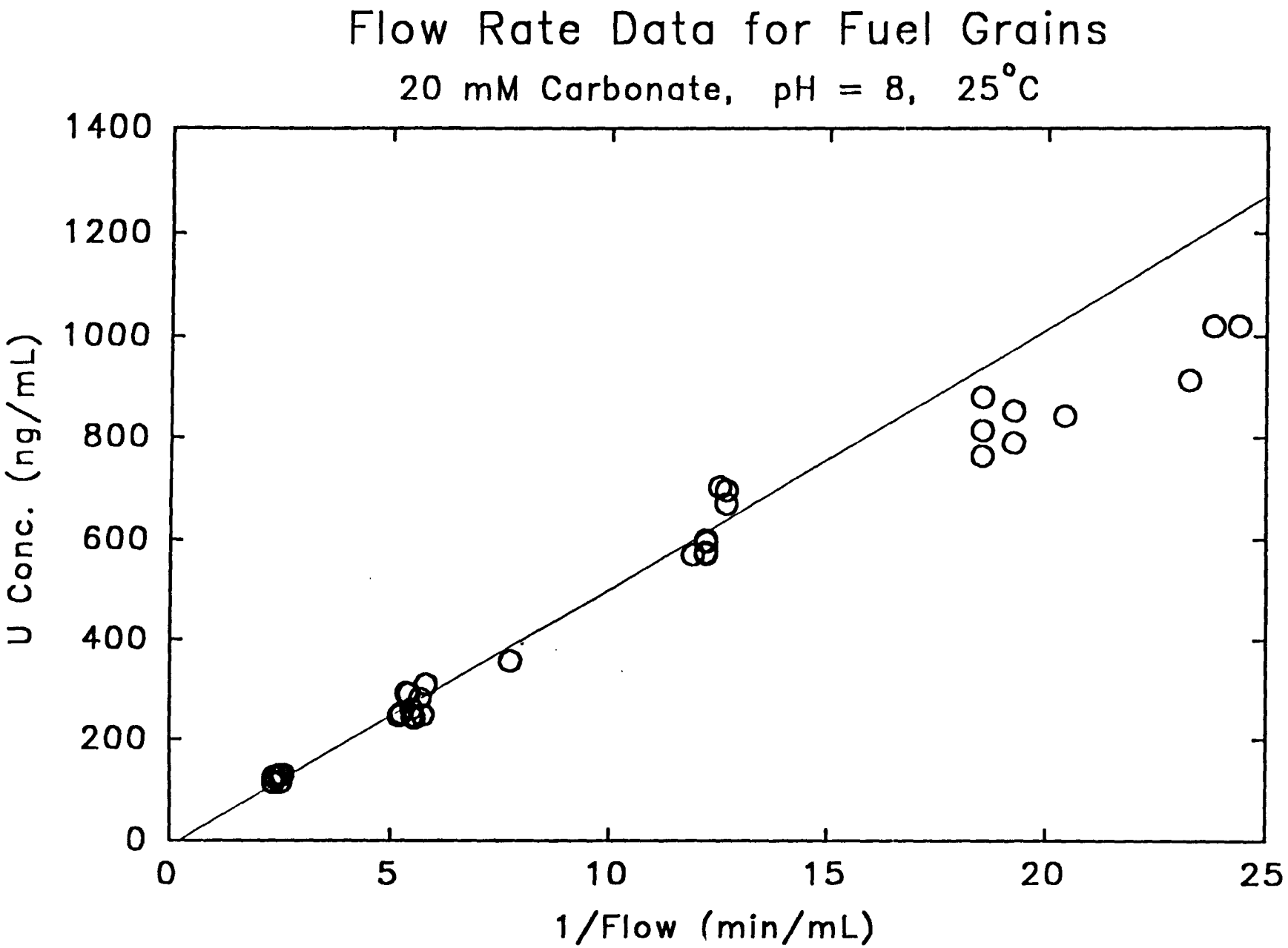
Spent Fuel Dissolution Testing

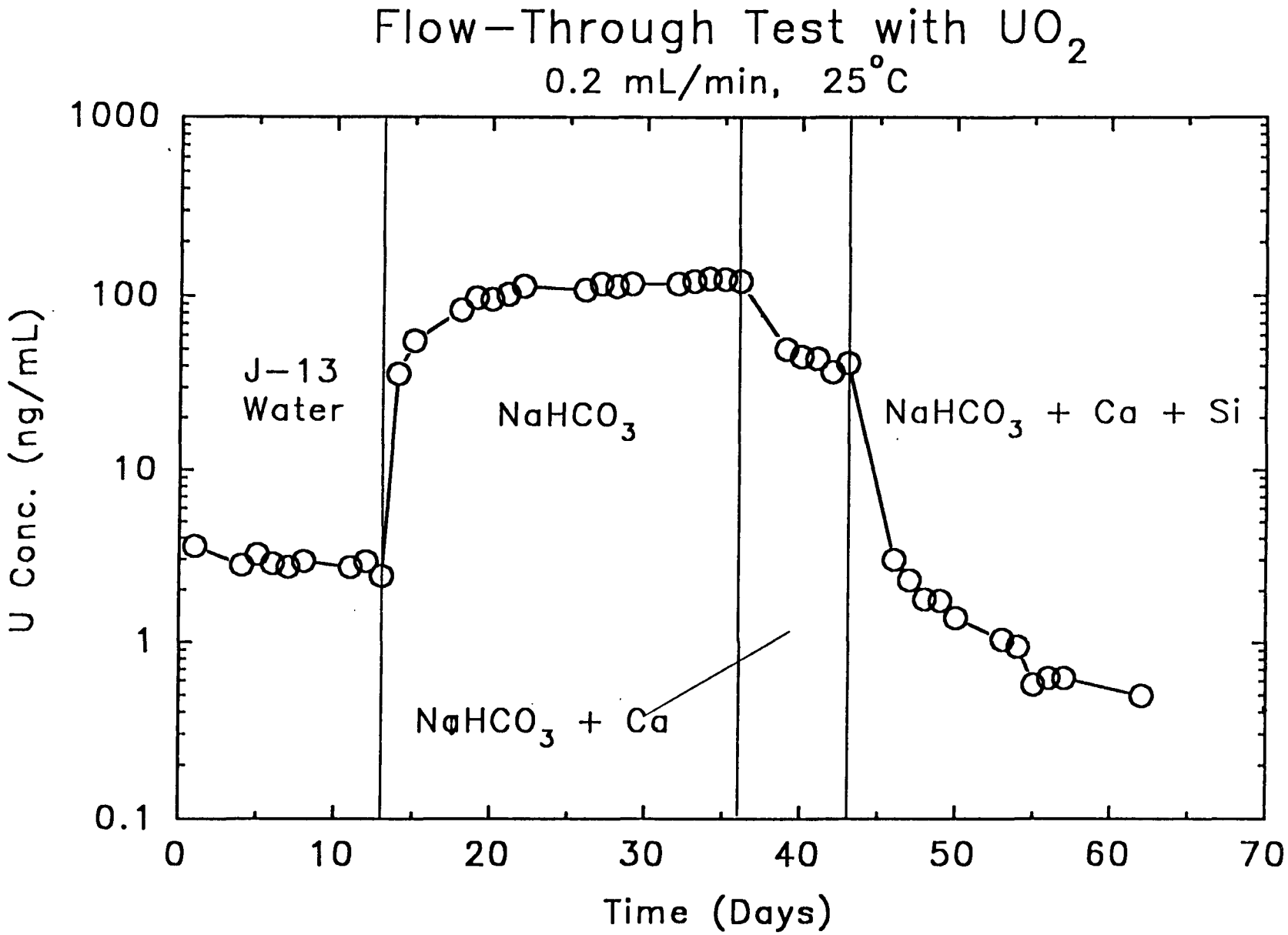


Radiochemical Analyses:

- U by Laser Fluorimetry
- ^{137}Cs by Direct Gamma Counting
- ^{99}Tc and ^{90}Sr by Chemical Separation Followed by Beta Counting


Dissolution Rate of Fuel Grains
20 mM Carbonate, pH = 8, 25°C
Fraction per Day (X 10^4)
U Normalized Rate (mg/m^2/day)
Time (days)
U
137Cs
99Tc
90Sr
0
2
4
6
8
10
12
0
20
40
60
80
100
120
140
160

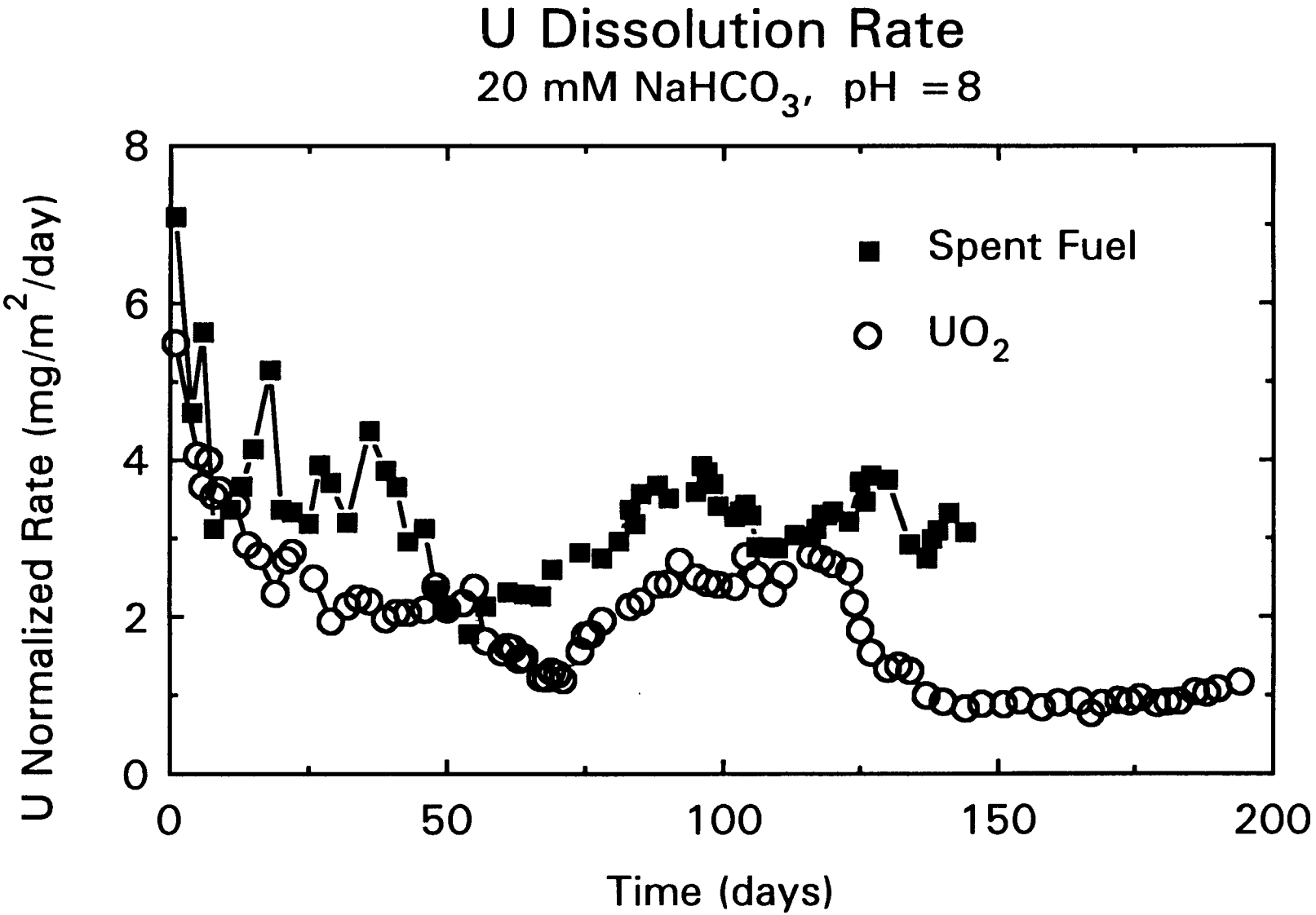

Flow Rate Data for Fuel Grains
20 mM Carbonate, pH = 8, 25°C
U Conc. (ng/mL)
1400
1200
1000
800
600
400
200
0
0
5
10
15
20
25
1/Flow (min/mL)


Flow–Through Test with UO_2
0.2 mL/min, 25°C
U Conc. (ng/mL)
1000
100
10
1
0.1
0
10
20
30
40
50
60
70
Time (Days)
J–13 Water
$NaHCO_3$
$NaHCO_3$ + Ca + Si
$NaHCO_3$ + Ca

ACCOMPLISHMENTS '87 - '92 (Continued)

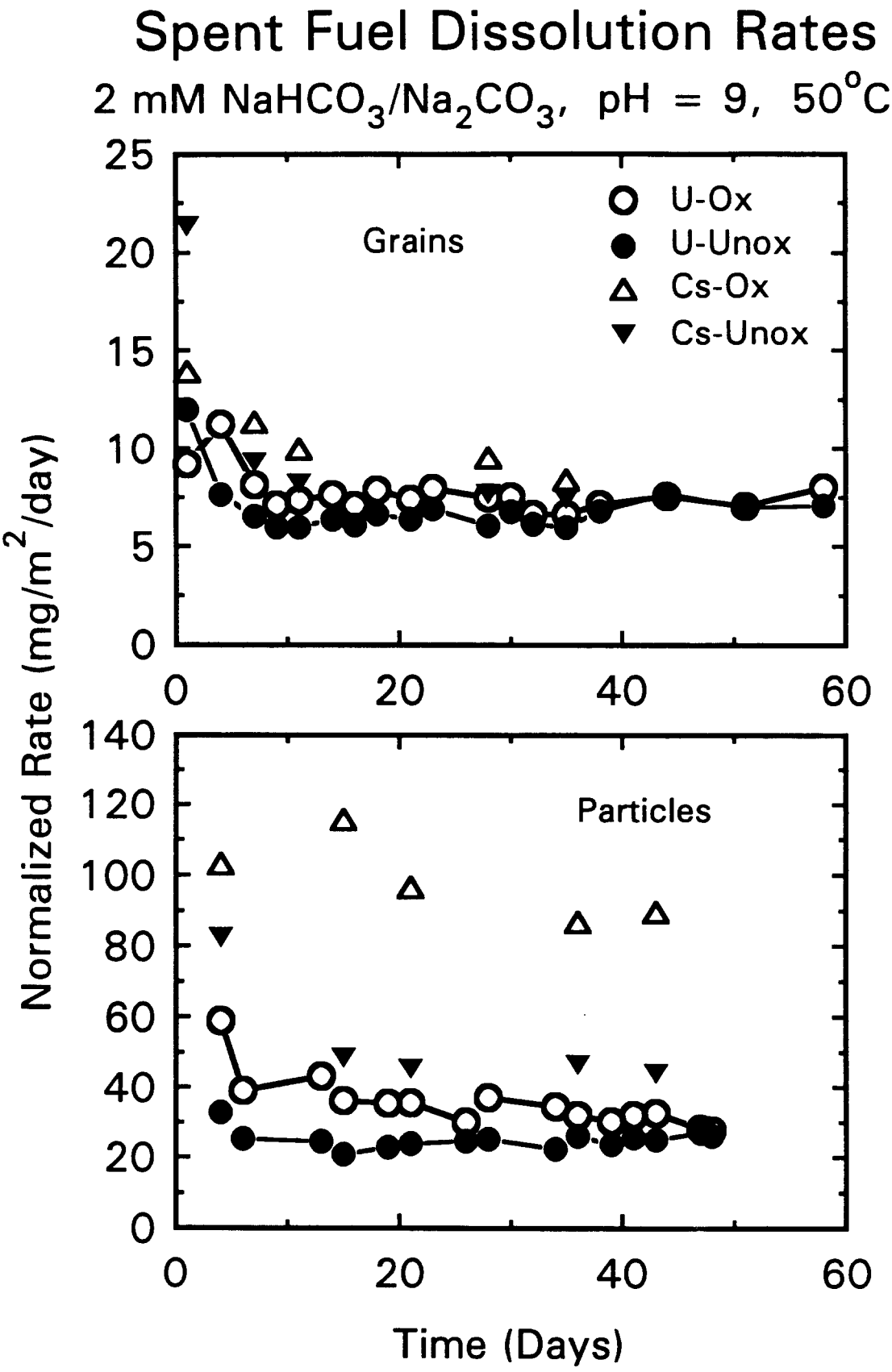
- Developed dissolution test matrix (UO_2 at LLNL; spent fuel at PNL) to investigate:

  * temperature (25 to 75°C)
  * carbonate/bicarbonate concentration (2×10^{-4} to 2×10^{-2} M)
  * pH (8 to 10)
  * oxygen fugacity (20% to 0.2%)


U Dissolution Rate
20 mM NaHCO3, pH =8
U Normalized Rate (mg/m2/day)
Time (days)
Spent Fuel
UO2
0
2
4
6
8
0
50
100
150
200

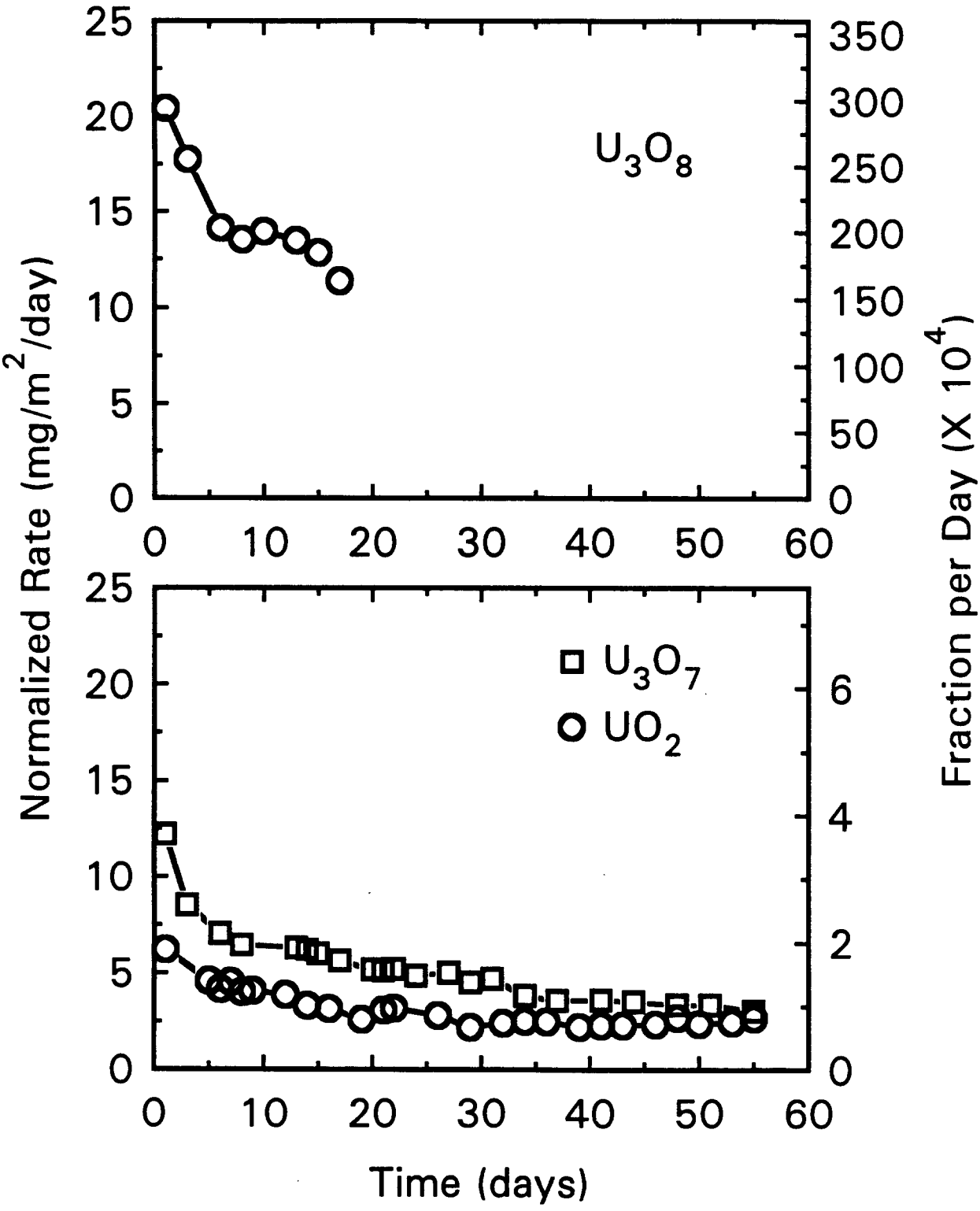
ACCOMPLISHMENTS '87 - '92 (Continued)

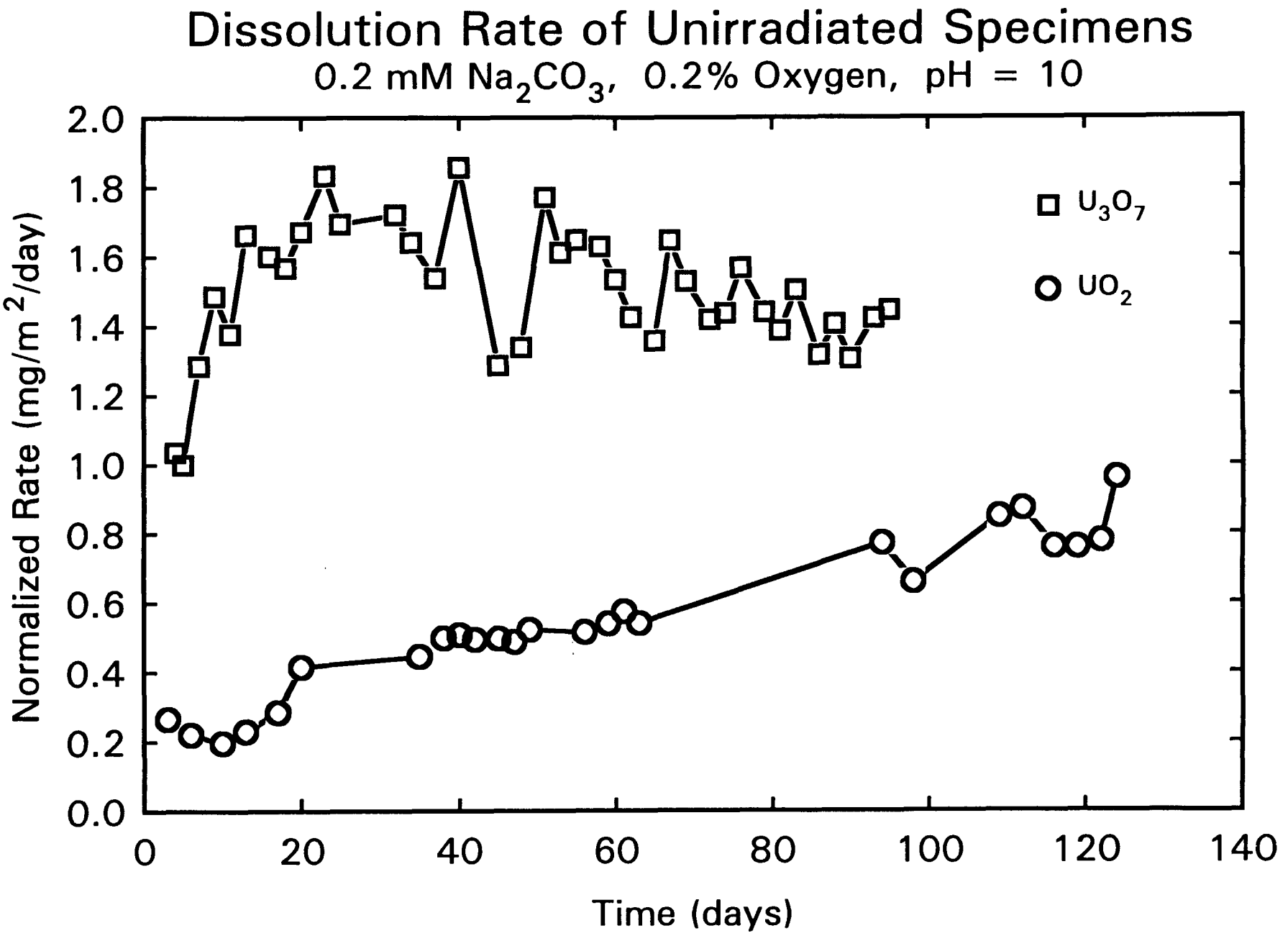
- For a limited number of fuels and test conditions, showed that dissolution rates of unirradiated UO_2 and spent fuel up to burnup of 50 MWd/kgM are roughly equal.
- For one fuel and one test condition, showed that dissolution rates of spent fuel oxidized to U_4O_{9+x} ($UO_{2.4}$) are roughly equal to those of unoxidized fuel.
- For one test condition, showed that dissolution rates of unirradiated UO_2 and U_3O_7 are roughly equal.
- For one test condition, showed that dissolution rates of unirradiated U_3O_8 are much higher than UO_2.
- For one fuel and one test condition, demonstrated that flow-through fractional dissolution rates are not substantially different from those in semi-static tests.

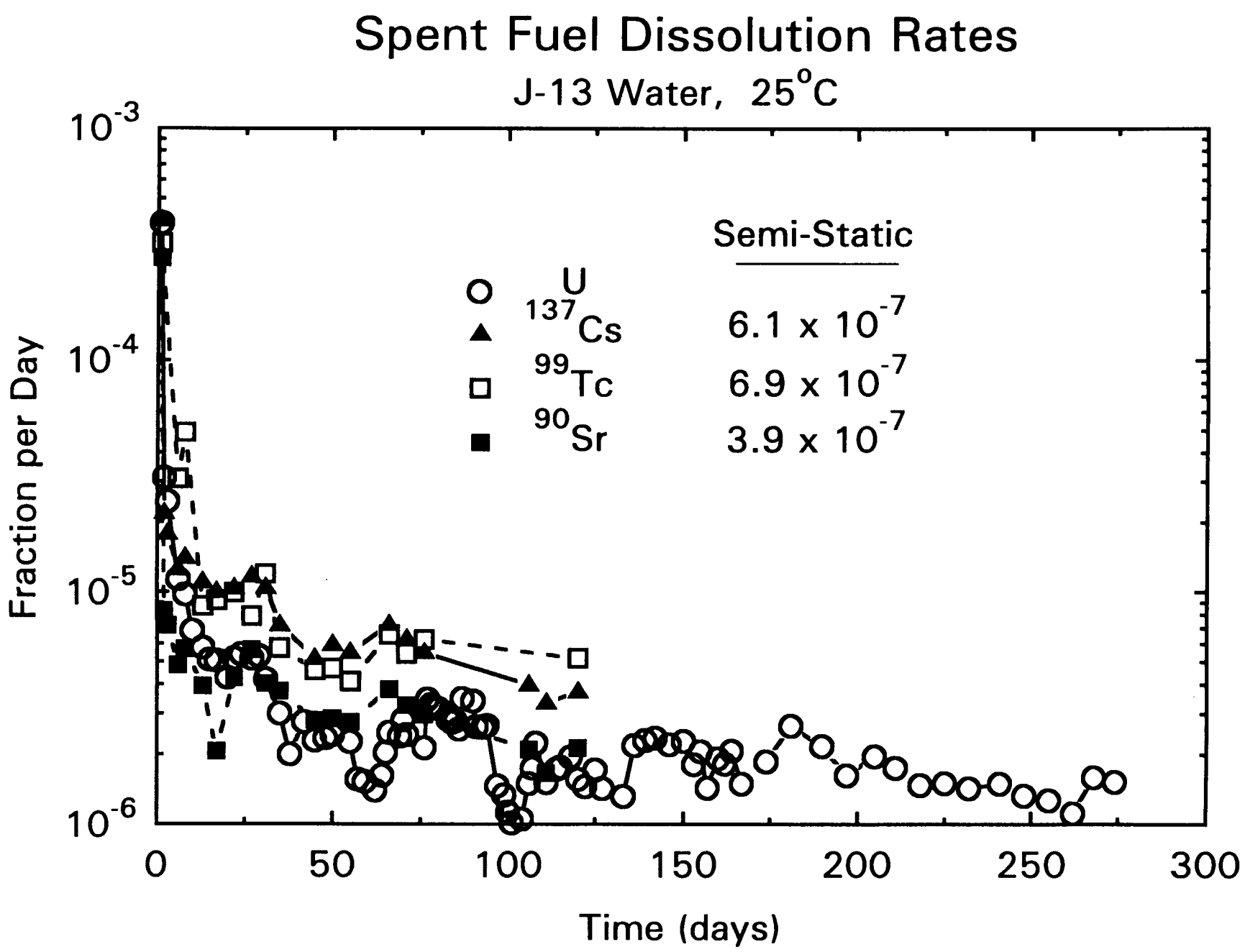

Spent Fuel Dissolution Rates
2 mM NaHCO3/Na2CO3, pH = 9, 50°C
Grains
U-Ox
U-Unox
Cs-Ox
Cs-Unox
Particles
Normalized Rate (mg/m2/day)
Time (Days)
0
5
10
15
20
25
0
20
40
60
0
20
40
60
80
100
120
140

Dissolution Rate of Unirradiated Specimens

20 mM $NaHCO_3$, pH = 8




Dissolution Rate of Unirradiated Specimens
0.2 mM Na_2CO_3, 0.2% Oxygen, pH = 10
Normalized Rate (mg/m^2/day)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
100
120
140
Time (days)
U_3O_7
UO_2


Spent Fuel Dissolution Rates
J-13 Water, 25°C
Semi-Static
U
137Cs
6.1 x 10-7
99Tc
6.9 x 10-7
90Sr
3.9 x 10-7
Fraction per Day
10-3
10-4
10-5
10-6
0
50
100
150
200
250
300
Time (days)

SUMMARY OF ACCOMPLISHMENTS

- Showed that solubility constraints are likely to limit release of actinides (over 98% of total activity) to far less than 1 part in 100,000 per year unless colloids make an important contribution.

- Developed method for measuring grain-boundary inventories and showed, for the two fuels tested, that the inventories of Cs, Sr, and Tc are quite small.

- Developed method for measuring the dissolution rate of the UO_2 matrix in spent fuel and demonstrated (only 3 fuels) that it dissolves congruently.

- For a very limited number of fuels and test conditions, showed that oxidation (up to $UO_{2.4}$ and U_3O_7) and burnup (unirradiated up to 50 MWd/kgM) have little effect on dissolution rates under the conditions tested.

SUMMARY OF ACCOMPLISHMENTS (Continued)

- For a single fuel and test condition, showed that dissolution rates in flow-through tests are not substantially different from those observed in semi-static (more repository relevant) tests.
- Showed that the presence of Si or Ca in test solutions has an important influence on dissolution rates.
- Embarked on systematic test program to determine the effects of various parameters on the dissolution rate of the UO_2 matrix of spent fuel.

GOALS FOR FY-1993 AND BEYOND

1) Generate thermodynamic data for key solid/solution reactions involving low-solubility radionuclides.

2) Work to identify solid phases that control the solubilities of the actinides under expected repository conditions.

3) Develop experiments to determine the nature and importance of actinide-bearing colloids.

GOALS (Continued)

4) Gap and grain-boundary inventory measurements.

- Extend measurements to a variety of fuels to correlate inventories with other fuel parameters such as burnup and fission gas release.

5) Flow-through dissolution-rate measurements.

- Measure dissolution rates for spent fuel oxidized beyond $UO_{2.4}$.
- Measure dissolution rates for oxidized spent fuel under other water chemistry test conditions. Also test additional oxidized fuels.
- Complete current test matrix with UO_2 and spent fuel.
- Expand test matrix to include Si, Ca, and waste package corrosion products.
- Extend measurements to gadolinia fuels and fuels with very high burnup.

PUBLICATIONS

C. N. Wilson, Results from NNWSI Series 1 Spent Fuel Leach Tests, HEDL-TME 84-30, Westinghouse Hanford Co., Richland, WA, 1985.

V. M. Oversby and C. N. Wilson, "Derivation of a Waste Package Source Term for NNWSI from the Results of Laboratory Experiments," Sci. Basis for Nucl. Waste Management IX. Vol. 50, ed. L. O. Werme, pp. 337-346. Materials Research Society, Pittsburgh, PA, 1986.

C. N. Wilson and H. F. Shaw, "Experimental Study of the Dissolution of Spent Fuel at 85°C in Natural Ground Water." Sci. Basis for Nucl. Waste Management X. Vol. 84, ed. J. K. Bates and W. B. Seefeldt, pp. 123-130. Materials Research Society, Pittsburgh, PA, 1987.

C. N. Wilson, "Summary of Results from the Series 2 and Series 3 NNWSI Bare Fuel Dissolution Tests." Sci. Basis for Nucl. Waste Management XI. Vol. 112, ed. M. J. Apted and R. E. Westerman, pp. 473-483. Materials Research Society, Pittsburgh, PA, 1988.

C. N. Wilson, Results from NNWSI Series 2 Bare Fuel Dissolution Tests, PNL-7169, Pacific Northwest Laboratory, Richland, WA, 1990.

C. N. Wilson, Results from NNWSI Series 3 Spent Fuel Dissolution Tests, PNL-7170, Pacific Northwest Laboratory, Richland, WA, 1990.

C. N. Wilson and W. J. Gray, "Effects of Water Composition on the Dissolution Rate of UO_2 Under Oxidizing Conditions." High Level Radioactive Waste Management Proceedings of the First International Conference. pp. 1431-1436. American Nuclear Society, Inc. La Grange Park, Il, 1990.

Publications (Continued)

C. N. Wilson and W. J. Gray, "Measurement of Soluble Nuclide Dissolution Rates from Spent Fuel." Sci. Basis for Nucl. Waste Management XIII. Vol. 176, ed. V. M. Oversby and P. W. Brown, pp. 489-498. Materials Research Society, Pittsburgh, PA, 1990.

W. J. Gray, D. M. Strachan, and C. N. Wilson, "Gap and Grain-Boundary Inventories of Cs, Tc, and Sr in Spent LWR Fuel." Presented at The XV International Symposium on the Scientific Basis for Nuclear Waste Management, November 4-8, 1991 in Strasbourg, France, 1991.

W. J. Gray and D. M. Strachan, "UO_2 Matrix Dissolution Rates and Grain-Boundary Inventories of Cs, Sr, and Tc in Spent LWR Fuel." Sci. Basis for Nucl. Waste Management XIV. Vol. 212, ed. T. A. Abrajano, Jr. and L. H. Johnson, pp. 205-212. Materials Research Society, Pittsburgh, PA, 1991.

C. N. Wilson, 1991. "Results from Long Term Dissolution Tests Using Oxidized Spent Fuel." Sci. Basis Nuc. Waste Manag. XIV. Vol. 212, ed. T. Abrajano, Jr. and L. H. Johnson, pp. 197-204. Materials Research Society, Pittsburgh, PA, 1991.

W. J. Gray and L. E. Thomas, "Dissolution Rates of As-Received and Partially Oxidized Spent Fuel." High-Level Radioactive Waste Management: Proceedings of the Third International Conference. pp. 1458-1464. American Nuclear Society, Inc. La Grange Park, Il, 1992.

W. J. Gray, L. E. Thomas, and R. E. Einziger, "Effects of Air Oxidation on the Dissolution Rate of LWR Spent Fuel." To be presented at the XIV International Symposium on the Scientific Basis for Nuclear Waste Management, November 30 - December 4, 1992 in Boston, MA.